REPORT DOCUMENTATION PAGE			*Form Approved* *OMB No. 0704-0188*

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
10/19/2015	Final Report	1 Jan 2009 - 31 Jul 2015

4. TITLE AND SUBTITLE Minimally Adhesive, Advanced Non-toxic Coatings of Dendrimeric Catalysts in Sol-Gel Matrices	5a. CONTRACT NUMBER
	5b. GRANT NUMBER N00014-09-1-0217
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Detty, Michael R.	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) THE RESEARCH FOUNDATION OF THE STATE UNIVERSITY OF NEW YORK DBA SUNY AT BUFFALO OFFICE OF SPONSORED PROGRAMS 402 CROFTS HALL	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 875 North Randolph Street Arlington, VA 22203-1995	10. SPONSOR/MONITOR'S ACRONYM(S) ONR
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution is Unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
We have developed new xerogel coatings with organochalcogenide or metal oxide catalysts for the activation of hydrogen peroxide as anti-fouling, fouling-release surfaces. The catalysts perform more efficiently when covalently attached to the xerogel framework. The use of organosiloxanes allows the preparation of organically modified xerogel surfaces with tunable surface energy, porosity/roughness, and topography. The use of longc-hain fluorocarbons allows the generation of phase separated materials with antifouling/fouling-release characteristics.

15. SUBJECT TERMS
anti-fouling, fouling-release, xerogel surfaces, peroxide catalysts, settlement, fouling removal

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Michael R. Detty
					19b. TELEPHONE NUMBER *(Include area code)*
U	U	U	UU	6	716-645-4228

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

20151027038

Final Technical Report for ONR N00014-09-1-0217

Minimally Adhesive, Advanced Non-toxic Coatings of Dendrimeric Catalysts in Sol-Gel Matrices

Michael R. Detty, PI/PD

Summary of Research Highlights Supported by ONR N00014-09-1-0217

1) Hydrophobic xerogel coatings are "robust" – good adhesion to glass, aluminum, fiberglass. Coated boats are in third and fourth seasons following application with no apparent deterioration of performance.
2) Xerogel surfaces with uniform topography are good models for correlation of surface energy/critical surface tension/water contact angles with settlement of fouling organisms/materials and strength of adhesion of fouling organisms/materials.
3) Xerogels incorporating TFPTMOS, PhTEOS, C3TMOS, C8TEOS, TEOS combinations give reduced settlement of *B. amphitrite* cyprids and zoospores of *Ulva linza* relative to PDMSE. *Ulva* sporelings are removed at hydrodynamic pressure comparable to PDMSE from the C18/C8/TEOS, 1:1 C3/TEOS, 1:1 C8/TEOS, 1:1:2 TFP/C3/TEOS, 1:1:2 TFP/C8/TEOS, and 1:1:2 C8/PH/TEOS xerogel formulations.
4) Statistically significant differences were noted with the various amine-containing xerogels with respect to settlement of zoospores of *Ulva*, removal of 7-day sporeling growth of *Ulva*, settlement of cypris larvae of the barnacle *B. amphitrite*, and removal of the diatom *Navicula perminuta* Low molar concentrations of long-chain alkyl trialkoxysilanes in combination with C8/TEOS show foul-release characteristics with removal of juvenile barnacles and algal sporelings. This may be a consequence of the formation of nanopores on the surface of the xerogel.
5) Leachate studies show that none of the xerogels leach materials that cause increased mortality relative to leachates from glass slides.
6) Xerogels can be tailored to provide improved foul-release performance through the introduction of topographical features and chemical inhomogeneities using long-chain-length alkyls and perfluoroalkyls in the siloxanes.
7) Novel catalysts for the activation of hydrogen peroxide have been prepared by incorporating the imidazolium group from an ionic liquid into a selenoxide or seleninic acid catalyst. These hybrid catalysts obviate the need for an ionic liquid – rates in aqueous media and ionic liquids are identical.
8) Peroxide catalysts that are an integral part of the xerogel framework (Si-C bond) are superior to catalysts that incorporate the catalyst as an alkoxy ligand.
9) The incorporation of low levels of PEG into TDF/TEOS xerogels leads to porous structures with high surface area, high surface roughness, and chemical segregation of functionality.
10) Monoliths of 5 mole-% V_2O_5 or O=V(O-*i*Pr)$_3$ in tetraethoxysilane (TEOS)-based xerogels containing 1 mole-% MW 3200 PEG or 1 mole-% 3-aminopropyltriethoxysilane (APTES) displayed catalytic activity comparable to the most active organochalcogenide catalysts.
11) In solution, diaryl ditellurides are the most active catalysts for the activation of H_2O_2 that have been examined in our studies. The active catalyst was identified as the tellurinic acid.

12) Topographical features such as nano- and micropores, and regions of chemical inhomogeneity produced selectively by judicious use of long-chain alkylsiloxane, perfluorosiloxane and PEG precursors have been examined chemically using TERS (tip-enhanced Raman spectroscopy).

13) A suite of xerogels with diverse properties (surface energy, charge, topography) have identified properties that either minimize or maximize settlement and removal of fouling species and biopolymers such as proteins.

Publications Citing ONR N00014-09-1-0217 for Support

1) Bennett, S. M.; Finlay, J. A.; Gunari, N.; Wells, D. D.; Meyer, A. E.; Walker, G. C.; Callow, M. E.; Callow, J. A.; Bright, F. V.; Detty M. R. The role of surface energy and water wettability in aminoalkyl/fluorocarbon/hydrocarbon-modified xerogel surfaces in the control of marine biofouling. *Biofouling* **2010**, *26*, 235-246.

2) Finlay, J. A.; Bennett, S. M.; Brewer, L. Sokolova, A.; Clay, G.; Gunari, N.; Meyer, A. E.; Walker, G. C.; Wendt, D. E.; Callow, M. E.; Callow, J. A.; Detty, M. R. Barnacle settlement and the adhesion of protein and diatom microfouling to xerogel films with varying surface energy and water wettability. *Biofouling* **2010**, *26*, 657-666.

3) Gunari, N.; Brewer, L. H.; Bennett, S. M.; Sokolova, A.; Kraut, N. D.; Finlay, J. A.; Meyer, A. E.; Walker, G. C.; Wendt, D. E.; Callow, M. E.; Callow, J. A.; Bright, F. V.; Detty, M. R. The control of marine biofouling on xerogel surfaces with nanometer-scale topography. *Biofouling* **2011**, *27*, 137-149.

4) Nascimento, V.; Alberto, E. E.; Tondo, D. W.; Dambrowski, D.; Detty, M. R.; Nome, F.; Braga, A. L. GPx-like activity of selenides and selenoxides: Experimental evidence for the involvement of hydroxy perhydroxy selenane as the active species. *J. Am. Chem. Soc.* **2012**, *134*, 138-141.

5) Sokolova, A.; Bailey, J. J.; Brewer, L. H.; Finlay, J. A.; Fornalik, J.; Wendt, D. E.; Callow, M. E.; Callow, J. A.; Bright, F. V.; Detty, M. R. Spontaneous multiscale phase separation within fluorinated xerogel coatings for fouling-release surfaces. *Biofouling*, **2012**, *28*, 143-157.

6) Sokolova, A.; Cilz, N.; Daniels, J.; Stafslien, S. J.; Brewer, L. H.; Wendt, D. E.; Bright, F. V.; Detty, M. R. A comparison of antifouling/foul-release characteristics of non-biocidal xerogel and commercial coatings toward micro- and macrofouling organisms. *Biofouling* **2012**, *28*, 511-523.

7) Alberto, E. E.; Braga, A. L.; Detty, M. R. Imidazolium-containing diselenides for catalytic oxidations with hydrogen peroxide and sodium bromide in aqueous solutions. *Tetrahedron* **2012**, *68*, 10476 – 10481.

8) Evariste, E.; Gatley, C. M.; Detty, M. R.; Callow, M. E.; Callow, J. A. The performance of aminoalkyl/fluorocarbon/hydrocarbon-modified xerogel coatings against the marine alga *Ectocarpus crouaniorum*: relative roles of surface energy and charge. *Biofouling* **2013**, *29*, 171-184.

9) Balkrishna, S. J.; Kumar, S.; Azad, G. K.; Bhakuni, B. S.; Panini, P.; Ahalawat, N.; Tomar, R. S.; Detty, M. R.; Kumar, S. An ebselen like catalyst with enhanced GPx activity via a selenol intermediate. *Org. Biomol. Chem.* **2014**, *12*, 1215-1219.

10) Detty, M. R.; Ciriminna, R.; Bright, F. V.; Pagliaro, M. Environmentally benign sol-gel antifouling and foul-releasing coatings. *Acc. Chem. Res.* **2014**, *47*, 678-687.

11) Alberto, E. E.; Muller, L. M.; Detty, M. R. Rate accelerations of bromination reactions with NaBr and H_2O_2 via the addition of catalytic quantities of diaryl ditellurides. *Organometallics* **2014**, *33*, 5571-5581.

12) Destino, J.; Gatley, C.; Craft, A.; Detty, M. R.; Bright, F. V. Probing nanoscale chemical segregation and surface properties of antifouling hybrid xerogel films. *Langmuir*, **2015**, *31*, 3510-3517.

13) Gatley, C. M.; Muller, L. M.; Lang, M. A.; Alberto, E. E.; Detty, M. R. Xerogel-Sequestered Silanated Organochalcogenide Catalysts for Bromination with Hydrogen Peroxide and Sodium Bromide *Molecules* **2015**, *20*, 9616-9639.

14) Pagliaro, M.; Detty, M. R.; Bright, F. V.; Ciriminna, R. Xerogel coatings produced by the sol-gel process as anti-fouling, fouling-release surfaces: from lab bench to commercial reality. *ChemNanoMat,* **2015**, *1*, 148-154.

Patents Supported by ONR N00014-09-1-0217

1) Detty, M. R.; Drake, M. D.; Tang, Y.; Bright, F. V. “Hybrid Anti-fouling Coating Compositions and Methods for Preventing the Fouling of Surfaces Subjected to a Marine Environment,” *US Patent* 7,794,795 B2 (Sep, 2010).

2) Detty, M. R.; Bright, F. V.; Bennett, S. M.; Sokolova, A. "Antifouling Coating Compositions and Methods For Preventing the Fouling of Surfaces," *US Application* 61/494,924 (June, 2011).

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4) Detty, M. R.; Calitree, B.; Eisenberg, R.; McCormick, T.; Orchard, A. “Chalcogenoxanthylium Dyes as Photosensitizers for Evolution of Hydrogen from Aqueous Solutions,” US Application 13/522,832 (July, 2012).

5) Detty, M. R.; Bright, F. V.; Cartwright, A.; Yung, K. Y.; Xu, H.; Liu, K. “Heavy Chalcogen Analogues of Rhodamine and Rosamine Dyes as Photoinitiators for Free-Radical Polymerization,” lEdison Number: 5992614-11-0016 (August, 2011).

Invited Presentations Citing ONR N00014-09-1-0217 for Support

1) Detty, M. R. “Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling,” ONR/AMBIO 2009 Workshop on Antifouling and Fouling Release Coatings, St. Petersburg, FL (2009).

2) Detty, M. R. “Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling,” Paquette Legacy Symposium 2010, The Ohio State University, Columbus, OH (May 15, 2010).

3) Detty, M. R. “Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling,” ONR/SEACOAT International Workshop, Las Vegas, NV (December, 2011).

4) Detty, M. R. “Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling,” Department of Chemistry, Elmira College, Elmira, NY (February, 2012).

5) Detty, M. R. “Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling,” 16th International Congress of Marine Corrosion and Fouling (ICMCF), Seattle, WA (June, 2012).

6) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," 38th Northeast Regional Meeting of the American Chemical Society, Symposium on Chemical Biology, Rochester, NY (October 2012).

7) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," Aquaculture 2013, Nashville, TN (Feb 25, 2013).

8) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," Department of Chemistry, University of Toronto, Toronto, Ontario, Canada (May 8, 2013).

9) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," Institute for Materials Science, University of North Carolina, Chapel Hill, NC (May 15, 2014).

Contributed Posters/Presentations Citing ONR N00014-09-1-0217 for Support (* denotes presenting author.)

1) Gatley, C.;* Evariste, E.; Callow, M. E.; Callow, J. A.; Detty, M. R. The Effects of Charged and Uncharged Xerogel Surfaces on the Adhesion Strength of the Brown Alga Ectocarpus Crouaniorum. ONR/SEACOAT International Workshop, Las Vegas, NV (2011).

2) Muller, L. M.; Alberto, E. E.; Sokolova, A.; Fornalik, J.; Detty, M. R. The Incorporation of Ionic Liquid Catalysts in the Xerogel Matrix: Effects on Surface Chemistry and Antifoul/Release Characteristics. ONR/SEACOAT International Workshop, Las Vegas, NV (2011).

3) Bailey, J. J.;* Sokolova, A.; Lang, M. A.; Brewer, L. H.; Wendt, D. E.; Fornalik, J.; Kraut, N.; Bright, F. V.; Detty, M. R. Analysis and IR Characterization of Four-component Xerogel Films as Antifouling and Foul Release Coatings. ONR/SEACOAT International Workshop, Las Vegas, NV (2011).

4) Alberto, E. E.;* Muller, L.; Detty, M. R. Imidazolium Ionic Liquids: Preparation and Evaluation as Components of Antifouling/Fouling-Release Coatings and as Catalysts for Oxidation of Bromide Salts with Hydrogen Peroxide in Water. ONR/SEACOAT International Workshop, Las Vegas, NV (2011).

5) Gatley, C. M.;* Detty, M. R.; Evariste, E.; Callow, M. E.; Callow, J. A. The Effects of Charged and Uncharged Xerogel Surfaces on the Adhesion Strength of the Brown Alga Ectocarpus Crouaniorum. 16th International Congress of Marine Corrosion and Fouling (ICMCF), Seattle, WA (June, 2012).

6) Gatley, C. M.; Detty, M. R.; Evariste, E.; Callow, M. E.; Callow, J. A. The Effects of Charged and Uncharged Xerogel Surfaces on the Adhesion Strength of the Brown Alga Ectocarpus Crouaniorum. 2012 Master's Level Graduate Research Conference, SUNY College at Brockport (April, 2012).

Degrees Awarded Based on Research Supported by ONR N00014-09-1-0217

1) Ms. Amber Bryant, University at Buffalo, M. A. in Chemistry, 2010, Thesis Title: *A Structure Activity Study of Sequestered Selenoxide Catalysts for the Activation of Hydrogen Peroxide as a Means to Eliminate Biofouling.*

2) Ms. Anastasiya Sokolova, University at Buffalo, M. Sc. in Medicinal Chemistry, 2011, Thesis Title: *Preparation and Analysis of Type II Xerogel Films with Antifouling/Foul Release Characteristics.*

3) Ms. Caitlyn Gatley, University at Buffalo, M. Sc. in Medicinal Chemistry, 2013, Thesis Title: *The Influence of Charged Xerogel Surfaces on the Settlement and Adhesion of Ectocarpus crouaniorum and Ulva linza.*

4) Ms. Lisa Muller, University at Buffalo, M. A. in Chemistry, 2015, Thesis Title: *The Kinetics and Recyclability of Telluride Catalysts Bound to Solid Silica and Their Potential for Environmentally Friendly Brominations.*

5) Dr. Stephanie M. Bennett, University at Buffalo, Ph. D. in Medicinal Chemistry, 2010, Dissertation Title: *Synthesis and Characterization of Sol-gel Derived Xerogel Films with Antifouling/Foul-release Properties and the Preparation, Immobilization, and Evaluation of a Selenoxide Catalyst for Brominations with Hydrogen Peroxide and Sodium Bromide in an Aqueous Environment.*

Postdoctoral Associates Conducting Research Supported by ONR N00014-09-1-0217

1) Dr. Sangit Kumar, 2009 – 2011, Chalcogenide catalysts for the activation of hydrogen peroxide.

2) Dr. Eduardo Alberto, 2012 – 2014, Chalcogenide catalysts for the activation of hydrogen peroxide.

Undergraduate Research Students (Two or More Semesters of Research Supported by ONR N00014-09-1-0217)

1) Mr. Vusumuzi Hove, B. Sc. in Chemistry, May, 2014
2) Ms. Meredith Lang, B. Sc. in Chemistry, December, 2013
3) Mr. Joseph Ferrar, B. Sc. in Chemical Engineering, May, 2011